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ATOMIC ABSORPTION ANALYSIS OF PHOSPHATES IN WATER

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ATOMIC ABSORPTION ANALYSIS OF PHOSPHATES IN WATER

by

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16. Abstract

The project investigated utilization of phosphate, silicate, and sulfate chemical inhibition effects in magnesium atomic absorption spectrometry for the purpose of determination of these anions. The variables found to be of greatest significance in the inhibition processes were flame temperature and solution stoichiometry. The procedure termed 'atomic absorption inhibition titration' (AAIT) was developed. It provides useful, new determination methods for single anions and also for simultaneous determination of phosphate, silicate, and sulfate in a single sample. The methods have been evaluated and applied to water and waste water samples. ~~(CAA)~~ (Booth-EPA)

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ABSTRACT

The project investigated utilization of phosphate, silicate and sulfate chemical inhibition effects in atomic absorption spectrometry for the purpose of determination of these anions. The magnesium atomic absorption signal was used. The variables found to be of greatest significance in the inhibition processes were flame temperature and solution stoichiometry. As a result of the latter, the procedure termed atomic absorption inhibition titration, AAIT, was developed. It involves constant rate addition of magnesium to the stirred sample solution while monitoring the latter solution for magnesium atomic absorption. Rather remarkable titration curve shapes are obtained, especially for solutions containing all three anions. Based on such titration curves, useful new determination methods were developed for single anions and also for simultaneous determination of the three anions present in a single sample.

The methods developed as applied to water and waste water have been investigated and found to be suitable in most respects and superior to present methods in some.

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CONCLUSIONS

1. New and improved analytical methods for analysis of common anions in water are achieved to meet the challenges of speed, accuracy, convenience, sample deterioration, precision, and cost.

2. Flame spectroscopic chemical inhibition effects can be a basis for such improved methods.

3. Flame temperature and solution ion ratios are the most significant parameters for utilizing the chemical inhibition methods. Solution ion ratios are most readily regulated by use of a titration technique.

4. Phosphate, silicate, and sulfate can be determined in real water and waste water samples, separated or in combination. A procedure requiring less than ten minutes allows the determination of these three anions in a single fifty milliliter sample.

5. Chemical inhibition processes in flames are shown to be rate controlled in the depleting droplet and resulting particle rather than controlled by solution equilibria.

6. The success in achieving these improved analytical methods indicates that further research should be pursued to exploit the above advances for water analysis problems of various types.

RECOMMENDATIONS

An advantageous new technique has been made available for water analysis. As a result, the following specific courses of action regarding it are recommended.

1. The method should be applied by a number of analytical chemistry laboratories for increased efficiency and for in-the-field evaluation of its capability.

2. The method should be completely automated by means of automatic sample handling and data acquisition and treatment computer equipment.

3. Simple minimal adequate design flame photometric apparatus should be developed or applied to exploit the cost and dependability advantages of the inherent simplicity of this new method.

4. The method should be extended to other anions, flame emission and fluorescence signals, and analysis of cations.

5. Finally, the technique provides a new tool for investigation of flame chemical inhibition reactions and very high temperature rate processes and stoichiometry. These capabilities should be applied to fundamental studies in these areas of chemistry.

INTRODUCTION

The importance for phosphate and other anion analysis is well-stated in an American Chemical Society report[1] on pollution abatment:

> Progress in analytical chemistry and instrumentation is vital to both water pollution research and survellance and research on eutrophication is a notable example of the need. The identification and measurement of limiting nutrients would be greatly eased by improved analytical methods for low levels of the forms of phosphorous compounds, the various forms of nitrogen compounds, trace metals, and trace organic growth factors in water.

Accordingly, the project objective was stated as follows:

> The initial aim is to determine phosphate in natural and waste waters by atomic absorption with high sensitivity, speed and specificity. The linear absorbance decrease for metals due to flame compound formation will be the observed quantity. The investigation will necessarily include studies of flame reaction stoichiometries and rates and should provide improved understanding of compound formation in flames. This will be used to establish a specific determination for the various phosphates as well as for other nonmetallic anions. The extension of the advantages of atomic absorption to analysis of many anions at concentrations present in natural waters is the final objective.

Present analytical methods for measurement of anions as outlined in Public Health Services' "Standard Methods of Water and Waste Water Analysis" are usually laborious and sometimes empirical. Interferences by silicate, arsenate, and other anions are troublesome. Because the methods are relatively slow errors sometimes enter during storage due to

micro organism action and adsorption effects. The above reference points out the desirability of fast field methods whenever possible.

A vast literature exists aimed at removing or minimizing chemical interference effects in flame spectroscopy. These effects of inhibiting anions due to formation of refractory species in the flame remain as probably the most important limitation on accuracy for most practical analysis of metals.[2]

In contrast, little has been reported on the use of these inhibitions as a means of analyzing the corresponding anions. The most common inhibiting anions are coincidentally also among the anions of most interest in natural and waste water chemistry and pollution studies, i.e., phosphate, sulfate, and silicate.

Studies in our laboratory have been aimed at obtaining specific inhibitions for each of these anions. Among the parameters investigated were: pH, beam height, fuel:oxidant ratio, burner type, total gas flow rate, and metal cation:inhibiting anion ratio. Among these parameters, fuel:oxidant ratio (i.e., flame temperature) and metal cation:anion ratio (i.e., solution stoichiometry) were found to be most useful.

To provide for convenient manipulation of solution stoichiometry as well as for an accurate analysis method

a titration procedure was adopted. We have termed the technique AAIT--atomic absorption inhibition titration. In this procedure the titrant, typically 100 µg/ml $MgCl_2$ is added by an infusion pump to 100 ml of the sample solution which contains 0.1 to 25 µg/ml of anion while the sample solution is being sampled by aspiration into the flame and the magnesium atomic absorption is monitored. Magnesium is selected as the monitor metal because of its sensitivity and its high extent of inhibition by refractory forming anions.

Atomic absorption inhibition titration (AAIT) has been successfully employed to determine phosphate, silicate, and sulfate as well as simultaneous determination of any combination of these anions in drinking and waste water.

EXPERIMENTAL

Methods based on inhibition effects require the use of relatively cool flames in which the compounds formed in the evaporating droplets are stable. The hydrogen-air flame provides conditions at which inhibition of these anions (SiO_2, PO_4, and SO_4) is realized without significant interference from less stable compounds. A number of experimental adjustments influence inhibition by anions. Inhibition ordinarily increases with excess of either fuel or oxidant gas flow, but decreases as beam height or total gas flow rate increases. These variables establish flame temperature in the light path. The optimized conditions for silicate determination has the combination of hydrogen flow rate of 10 ft^3/hr (30 psi), air, 10 ft^3/hr (40 psi) and for sulfate, 30 ft^3/hr (30 psi) for hydrogen and 10 ft^3/hr (30 psi) for air. The previous statement indicates a possibility to determine both silicate and sulfate anions at certain combinations of instrumental parameters with minimum interference from each other.

To obtain well characterized titration curves it is necessary to exchange cations with a hydrogen form ion exchange resin for standard as well as sample solutions, i.e., sodium and potassium ions impair sharpness of

titration signals. Such separations are accomplished in just a few minutes *via* a batch process because the ion concentrations involved are so low.

RESULTS

Phosphate Determination by AAIT: The anions selected in this study are ortho-, pyro-, tri-, tetra-, and hexa-phosphates. Observations were made with both total consumption and pre-mix slot burners. A hydrogen-air flame was used in order to have the relatively low flame temperatures and the flame temperature control which is necessary. The total consumption burner was a Jarrell-Ash "HETCO" model. The pre-mix burner had a 0.5 x 100 mm slot. For manual titration an ordinary glass buret was used with 0.027 in. I.D. plastic tubing leading into the titration solution in a 250-ml beaker stirred with a magnetic stirrer.

All solutions were prepared from reagent grade material using deionized distilled water (unless specified otherwise). Sodium hexametaphosphate and tetraphosphoric acid were commercial materials (Benlo Chemical Co.). To remove cations, the solution was treated with cation exchange resin (Dowex 50 x 8, 20-25 mesh) using a separatory funnel by a batch method. The cation exchange resin was exposed to dilute acid solution between uses.

Several detergent product brands were selected randomly from among those sold locally.

Before beginning a titration, gas flow rates were adjusted for maximum inhibition using a magnesium plus phosphate solution. The atomic absorption signal was observed at intervals during the titration by dipping the aspirator tube into the titration vessel. Steps were taken to insure that the titration solution level with reference to the burner did not change and that solution uptake rates were not sufficient to introduce significant errors. A complete manual titration curve was obtained in less than one-half hour. Semi-automatic titration requires less than five minutes.

Results for the total consumption burner inhibitions by the three anions, orthophosphate, silicate, and sulfate, were similar. The extent of inhibition was proportional to the magnesium absorption signal and generally followed the temperature profile of the flame.[3] Rather wide variation of hydrogen to air flow ratios (0.5 to 4.0) and total gas flow rates (15 to 50 ft^3/hr) showed little effect on the relative amounts of inhibition among the three anions. The degree of inhibition is similar for phosphate and silicate and is somewhat less for sulfate.

The inhibition effect is relatively linear with anion concentration for mole ratios of inhibitor (anion) to

absorber (Mg) less than unity and anion concentrations down to 0.5 μg/ml.

This linear response suggests the possibility of relatively precise and sensitive indirect measurement of these anions by their inhibiting effect. The specific analysis of one anion in the presence of the others is unlikely, however, because the relative inhibitions of sulfate, silicate, and phosphate are independent of vertical position, fuel to oxidant ratio, total gas flow rate, and anion concentration.

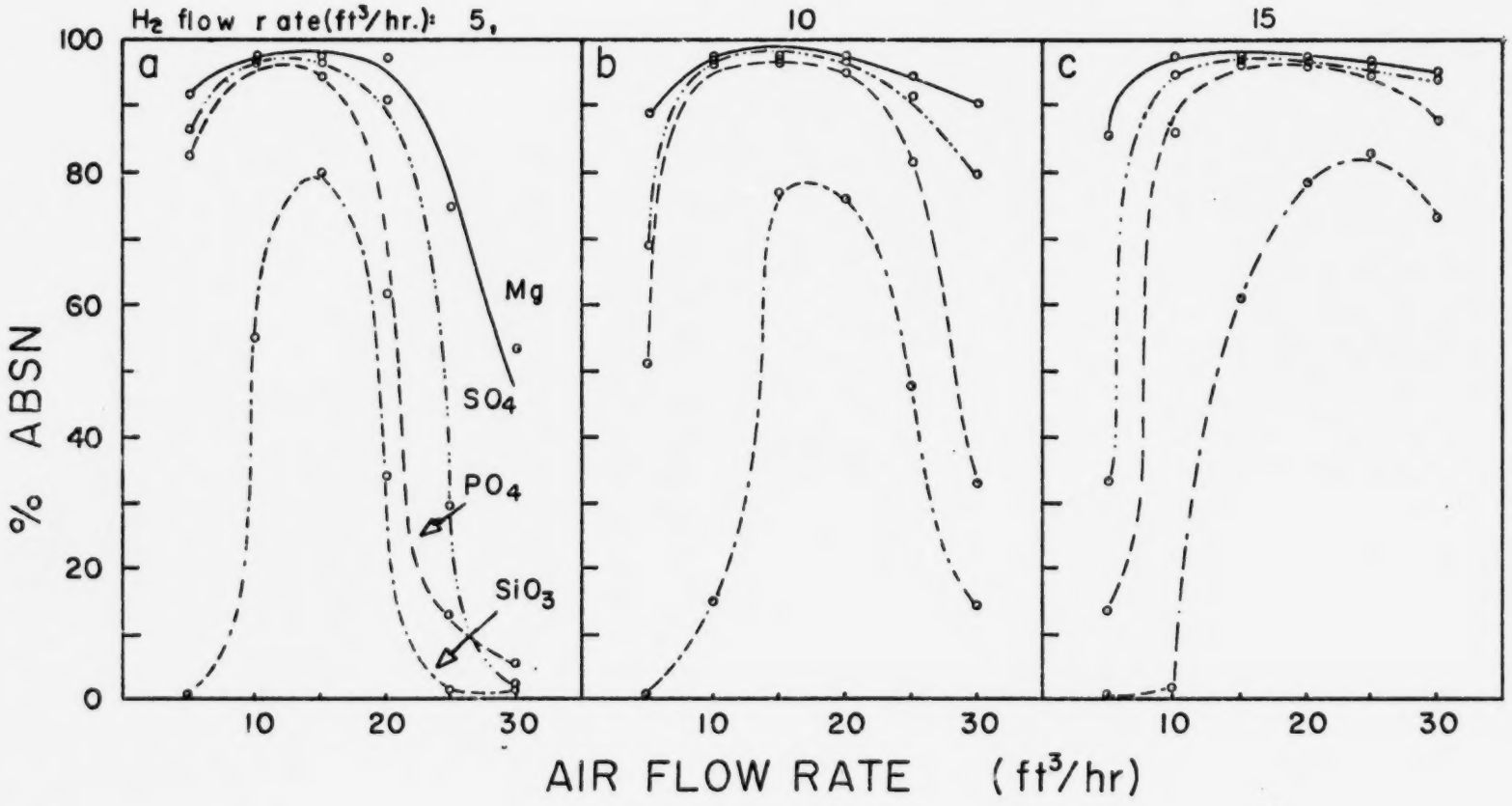
Data taken using a pre-mix burner are significantly different from those with the total consumption burner due to the smaller range of droplet sizes. Although with the latter, phosphate and silicate inhibited similarly, Figure 1 shows that with the pre-mix flame a progression in inhibition is observed. Inhibition for various fuel to oxidant flow rates is also shown in Figure 1. Several features of these plots are significant. Absorption by magnesium is at a maximum value and inhibitions are at or very near minimum values at hydrogen to air flow ratios near 2:5. This ratio corresponds to a stoichiometric mixture for combustion of hydrogen with air and thus a maximum in flame temperature. At lower or higher ratios the cooler flame results in more inhibition for all three anions, but also less absorption by magnesium. Observations for many more combinations of gas

Figure 1. Inhibition and Gas Flow Rates

Pre-mix burner

Burner height, 10 mm; λ = 285.2 nm; pH = 7

FIGURE 1



Conc: Mg 5ppm, Anions 20ppm

flow rates all yielded a similar pattern. When total gas flow rate is increased while maintaining constant hydrogen to air flow ratio the inhibition decreases due to the increased thermal input to the flame.

Inhibition for all three anions increases moderately with pH and with decreasing beam height in the flame. These trends were not distinctive for any one of the anions and were not considered suitable for application to selective determination of anions.

Data obtained here, in agreement with other workers,[2] show that when the mole ratio of inhibiting anion to metal exceeds approximately unity the extent of inhibition no longer increases on increasing the concentration of anion. At anion to magnesium mole ratios less than unity the occurrence of discontinuities in solution stoichiometry vs. absorption was observed for phosphate and silicate solutions. Titration permits convenient variation of the solution stoichiometry. Titration also allows easy maintenance of other experimental conditions during measurements. An example of a curve obtained when titrating phosphate with magnesium is shown in Figure 2. The remarkable shape of this curve forms the basis of the new measurement technique for low concentrations of phosphate. It represents a unique type of titration chemistry in that high temperature

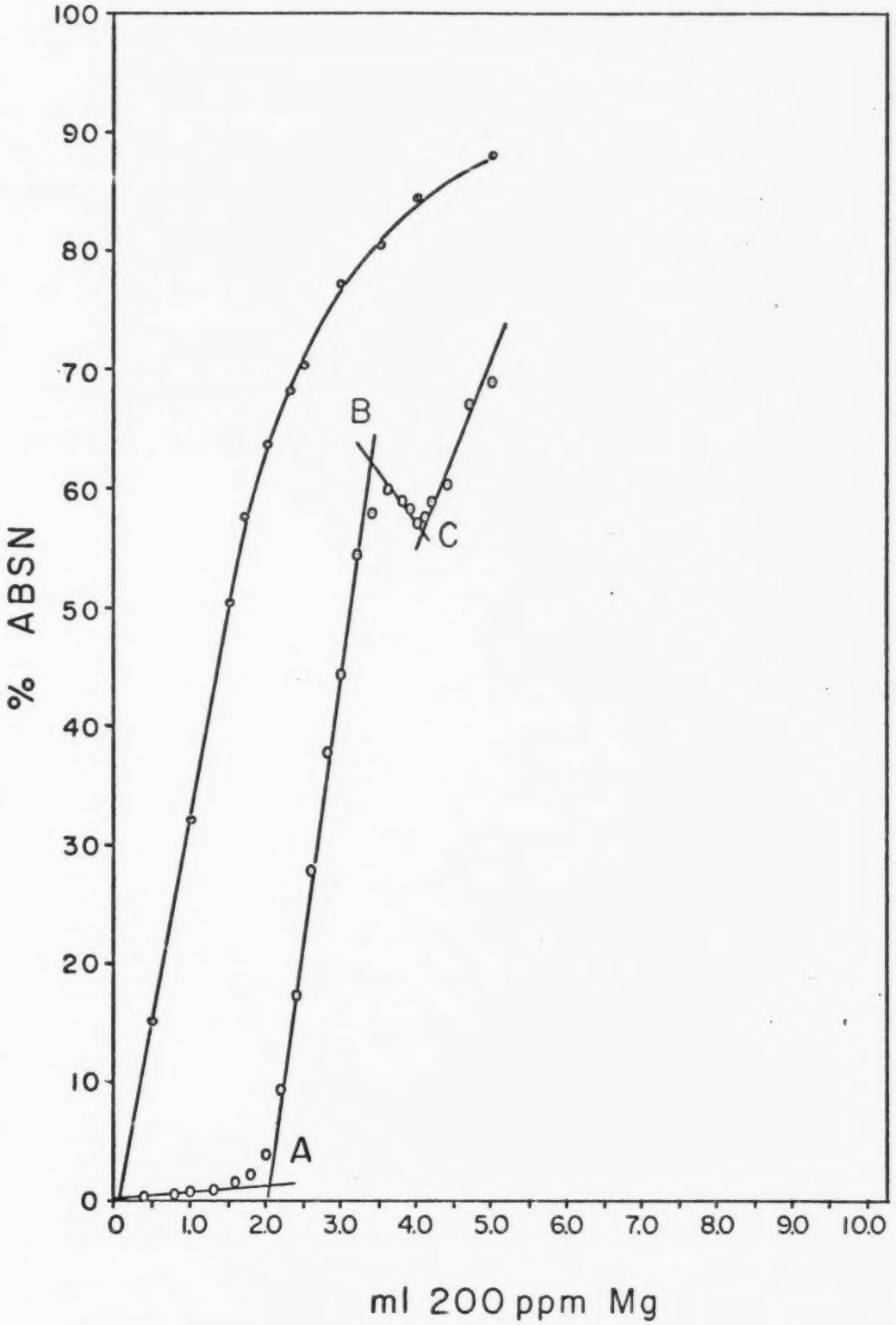
Figure 2. Titration of Blank and 8 ppm Orthophosphate

Titrant, $MgCl_2$ solution

Gas flow rates: Hydrogen, 25 ft^3/hr (60 psi)

Air, 5 ft^3/hr (80 psi)

FIGURE 2


100
90
80
70
60
50
40
30
20
10
0
% ABSN
B
C
A
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
ml 200 ppm Mg

processes on small bits of solution is the observed quantity. Reverse titrations of metals with inhibiting anions might also be advantageous in certain cases.

On the titration curve shown in Figure 2, points suitable for application to phosphate determinations are designated as A, B, and C. The shape of the curve combined with the titration data indicates that any of these points may be used for convenient endpoint designation. The three titration endpoints suggest refractory compound formations with approximately two, three, and four magnesium atoms per phosphorus atom. Such stoichiometries do not correspond to magnesium phosphate compounds or complexes of ordinary solution chemistry, but rather reflect high temperature processes occurring in the evaporating droplets.

The sample droplet is subject to drastic reactions including formation, dehydration, and volatilization of dry aerosol particles. All these processes occur in about one millisecond.[2] Stoichiometries quite different from those of ordinary solution chemistry are to be expected. The decreasing signal before point C can be assigned to a rate process involving formation of a more stable refractory species from a less stable initial species. The effect is even more prominent for solutions containing sulfate. This titration method allows investigation into the inhibition mechanisms.

Table I summarizes results for titrations of solutions containing sulfate as well as phosphate. The data show general agreement with titrations where no sulfate is present. The effects of sulfate on the titration curve were to decrease the absorption throughout the titration and to enhance the minimum at point C.

Polyphosphate Titrations: Polyphosphate titration curves had the same general shapes as those for orthophosphate. Titration stoichiometry was examined under the same instrumental settings as for phosphate titration. The endpoirts used corresponded to point A of Figure 2. The magnesium to phosphorus atom ratio appears to approach a constant atom ratio of unity with increasing size of the polyphosphate, whereas for orthophosphate the ratio is near two. These results suggest a kinetically determined inhibiting process in the droplets.

Silicate can be expected to interfere when present in samples. It must either be first separated or it must be determined by AAIT[4] and subtracted from total silicate and phosphate results.

Analysis of Milwaukee River water was performed in order to examine the utility of the analysis system. The slightly acidified sample was filtered through paper and

TABLE I

Titration PO_4/Mg Mole Ratios for Solutions Containing Phosphate and Sulfate

ppm PO_4	ppm SO_4	A	B	C
5	0	0.551	0.319	0.261
5	10	0.613	0.376	0.285
10	0	0.556		
10	5	0.527	0.297	0.244
10	10	0.551	0.321	0.263
10	15	0.538	0.366	0.289
15	10	0.602	0.334	0.248
		$\bar{x}$ = 0.562	0.336	0.262

then a 0.4 micron membrane filter. It was then passed through a cation exchange column in the acid form to replace naturally occurring magnesium, calcium, and other cations. The sample was diluted ten-fold for convenience. Titrations were performed on river water, river water plus standard addition of phosphate, and standardized phosphate solutions. The results are shown in Table II. Accuracy and precision are good considering the speed and sensitivity of the method. The absence of measurable silicates in the samples titrated was confirmed by observing a negligible endpoint for a titration at conditions under which only silicate would be detected. Thus, either the river water contained negligible dissolved silicate or silicate was quantitatively held in the cation exchanger. For best results, a standard addition must be titrated with the same flame adjustment and instrument settings used for the samples.

Phosphate determination was also performed on four brands of commercial detergent products (Table III). The detergent solutions were either boiled for one hour or aged for several days before titration.

Determination of sample No. 1 of the series of water analysis standard solutions offered by the Analytical Quality Control Laboratory yielded 0.050 (s = 0.001) ppm phosphorus compared with the stated value by AQCL of 0.05 ppm.

TABLE II

River Water Analysis

End Point			Concentration	
2 ppm PO_4 (ml)	River (ml)	River + 2 ppm PO_4 (ml)	PO_4 in River Water (ppm)	Added PO_4 Determined (ppm)
0.73	1.50	2.24	4.14	1.97
0.59	1.23	1.80	4.10	1.93
0.50	1.08	1.60	4.40	2.08
0.51	1.05	1.61	4.32	2.16
0.57	1.29	1.84	4.46	2.12
			$\bar{x}$ = 4.28	$\bar{x}$ = 2.05
			s = 0.16	s = 0.10

TABLE III

Determination of Phosphate in
Detergent Products by AAIT

Brand Number	PO_4 Found[a] (AAIT)	PO_4 Found (Std Method)
1	36.2 ± 0.5%	35.8%
2	36.1 ± 0.2%	36.5%
3	36.1 ± 0.5%	36.6%
4	28.9 ± 1.0%	24.6%

[a]Standard deviations based on five replicate titrations. Percent PO_4 in commercial material as received.

In conclusion, the results of this investigation indicate that atomic absorption inhibition titration (AAIT) is applicable to phosphate determination in surface and waste waters. A pre-mix burner is necessary for the AAIT method. When the phosphate solution is titrated with magnesium, three break points were found. At these points the magnesium to phosphate ratio remain essentially constant, and therefore can serve as the endpoints for titration, even in the presence of sulfate.

These details for AAIT determinations of phosphates are cited in reference 5.

Silicate Determination by AAIT: AAIT titration curves for silicate are of the same shape as those for phosphate. With use of a flame of sufficiently high temperature, silicate inhibits magnesium atomic absorption, but phosphate and sulfate do not. Accordingly, silicate can be determined in the presence of these ions in water samples. Typical data for such determination is given in Table IV. A report on silicate determination by this new method developed here is already in print[4].

TABLE IV

Determination of Silica in
Artificial Drinking Water

SiO_2 added (ppm)	SiO_2 det'nd (ppm)	Number of runs
0.50	0.54	2
1.00	1.00	2
2.00	2.06	1
3.00	3.09	1
4.00	3.77	1

$\bar{X}$ (mean µg SiO_2 found/µg SiO_2 present) = 1.02

s = 5.1%

Sulfate Determination by AAIT: Of the three anions considered here, sulfate has least tendency to undergo inhibiting reactions with magnesium in the droplets. Therefore, the AAIT determination of this anion requires use of a relatively cool flame. This was accomplished by using a fuel rich flame with hydrogen flow rate, 30 ft^3/hr, and air flow rate, 10 ft^3/hr. Inlet pressure to the flow meters was 30 psi. Under these conditions a simple titration curve is obtained in which a linearly increasing absorbance is observed beyond the titration endpoint. A linear extrapolation of this segment to the base line conveniently defines the endpoint. Typical data is indicated in Table V.

Determinations over a pH range of 1-9 resulted in no significant change in results obtained. Precision measurements on a 5 ppm SO_4 indicate a standard deviation of 0.2% for six determinations. Such titrations using 100 ppm Mg as titrant required less than 1.5 min to perform. Chloride, acetate, nitrate, and fluoride do not interfere; however, phosphate and silicate do interfere and must be removed. The latter two anions are much more basic than sulfate and so previous separation of them (e.g., ion exchange) is readily accomplished.

A report describing sulfate determinations by AAIT as developed in this project is already in print[6] and can be

TABLE V

Determination of Sulfate by AAIT

ppm SO_4 added	ppm SO_4 found
1.00	0.86
2.00	1.94
4.00	4.00
8.00	8.00
16.0	15.9
20.0	20.1

consulted.

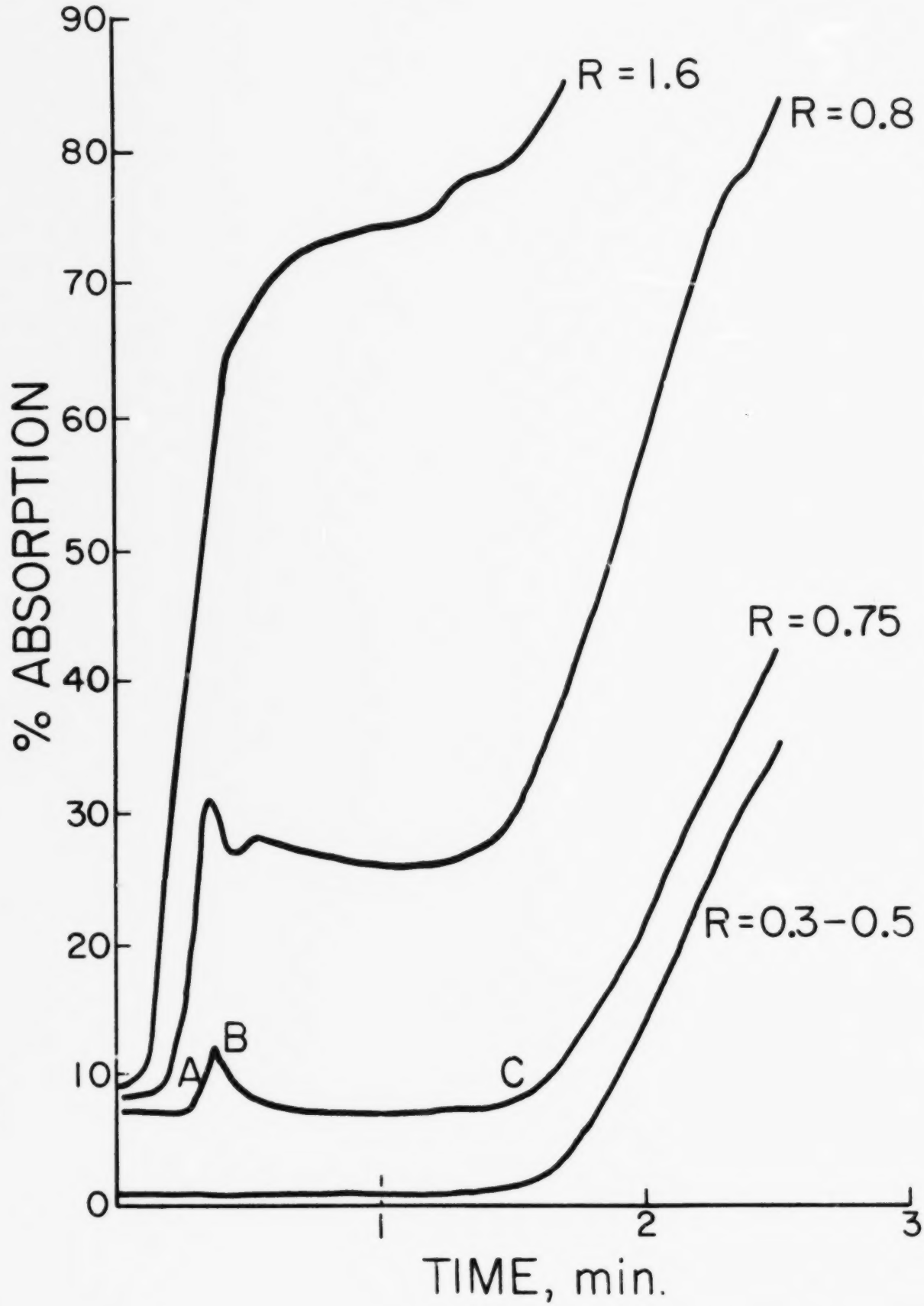
Simultaneous Determination of Anions by AAIT: Studies of AAIT curve shapes with more than one of the anions present indicated that with proper choice of flame conditions remarkably useful signals were obtained. Figure 3 shows titration curves obtained for solutions containing one µg/ml silicate and 25 µg/ml sulfate. Points A and B serve as endpoints for silicate and C minus B serves as the endpoint for sulfate. Figure 3 also shows data obtained for optimizing hydrogen to air flow ratios. Up to P = 0.5, this small amount of silicate does not show a titration signal, whereas at ratios greater than 1.5 the silicate signal predominates.

In order for simultaneous determination of silicate and sulfate together, the background intensity after the silica peak must be as low as possible without sacrificing the clarity of the silicate endpoint. The best condition for our work is hydrogen, 10 ft^3/hr (30 psi) and air, 7.5 ft^3/hr (30 psi). In the course of optimization we have used both the "Tri-Flame" pre-mix laminar flow burner head and the newer, improved teflon-lined burner head (Jarrell-Ash 82-374). It is found that the newer burner is more efficient in nebulizing solution.

Figure 3. Effect of Air:Hydrogen Flow Ratio, R, on Titration Curve

Hydrogen flow rate, 10 ft^3/hr (30 psi)

FIGURE 3


90
80
70
60
50
40
30
20
10
0
% ABSORPTION
R = 1.6
R = 0.8
R = 0.75
R = 0.3–0.5
A
B
C
1
2
3
TIME, min.

Simultaneous determination of silicate-sulfate system requires calibration standards for both components. These standards are least square fitted and show a linear correlation coefficient of 0.998 for 0.50 to 4.00 µg/ml SiO_2 in the presence of 20 µg/ml SO_4 and 0.984 for 5.00 to 30.0 µg/ml SO_4 in the presence of 1.0 µg/ml SiO_2. Thus, linear calibration for simultaneous determination of silicate and sulfate is possible.

This method has been applied to determine silicate and sulfate in raw water from Lake Michigan and drinking water from the Milwaukee Water Purification Plant. The results are summarized in Table VI. Data obtained by their laboratory using standard gravimetric methods are included for comparison. It is important to point out that the recovery of added one µg/ml silica in raw and effluent waters is almost 100% in the AAIT method even though the calibration curve was obtained in deionized distilled water. The small discrepancy between the standard gravimetric and AAIT methods was further investigated by synthesizing drinking water according to the data published by the American Chemical Society.[1]

The high accuracy and precision shown in Table IV lead to the conclusion that the AAIT method is valid for SiO_2 at these levels. The gravimetric data apparently contains

TABLE VI

Data Comparing AAIT and Gravimetric Methods

Sample	—Concentration of SO_4— (ppm)		—Concentration of SiO_4— (ppm)	
	AAIT Method[a]	Gravimetric Method[b]	AAIT Method[a]	Gravimetric Method[b]
Raw H_2O	21.5±0.1	20.7	1.39±0.04	1.2
Raw H_2O + 1.0 ppm SiO_2	21.7±0.5	--	2.41±0.05	---
Drinking H_2O	24.8±0.1	26.0	0.95±0.01	1.0
Drinking H_2O + 1.0 ppm SiO_2	25.3±0.2	--	2.03±0.03	---

[a]Deviations shown indicate range for two or three determinations. [b]As reported by Milwaukee Water Purification Plant.

negative error. Table IV indicates that the common anions present in drinking water do not interfere in the silica determination. A series of simultaneous titrations of samples containing various relative amounts of silicates and sulfate shows that the method is valid whenever the ratio of sulfate to silicate is larger than 2. A survey of data for municipal water supplies indicates that many fall into this category. Addition of known amounts of sulfate provides easy accomodation of those which do not.

Further investigations were aimed at even more general application to waste waters and at including phosphate in the analysis.

Data obtained for solutions containing silicate, sulfate, and phosphate showed that relatively linear relationships between points A, B, and C on the titration curve of Figure 3 were obtained as follows:

$$A = k_1[SiO_2] + b \qquad (1)$$

$$B = k_2[SiO_2] + k_3[PO_4] + b \qquad (2)$$

$$C = k_4[SiO_2] + k_5[PO_4] + k_6[SO_4] + b \qquad (3)$$

where bracketed terms indicate concentration.

A computer-assisted multiple linear regression analysis treatment of an array of experimental data resulted in evaluation of the coefficients in the set of equations:

$$[SiO_2] = K_1A + K_2 \quad (4)$$

$$[PO_4] = K_3B - K_4A - K_5 \quad (5)$$

$$[SO_4] = K_6C - K_7B + K_8A + K_9 \quad (6)$$

Thus a single titration for analysis of all three anions of interest is possible. Such titrations ordinarily require about five minutes to perform. Actual titration time is usually less than three minutes.

Data obtained for artificial waste water show that when total µg/ml of SiO_2 and PO_4 exceed one-half of µg/ml SO_4 the error ior SiO_2 and PO_4 determination becomes excessive. This is attributed to merging of points B and C of the titration curve (Figure 3). This limitation, however, does allow determination of most surface waters and many waste waters (See Table VII).

Again, a full report of the new method developed for simultaneous determination of the three anions in a single sample has been published[7].

TABLE VII

Simultaneous Determination of
SiO_2, PO_4, and SO_4 in Waste Water

Added (µg/ml)			Found (µg/ml)		
SiO_2	PO_4	SO_4	SiO_2	PO_4	SO_4
1.50	3.00	20.0	1.44	3.04	20.5
1.50	2.00	20.0	1.60	1.56	20.3
4.00	2.00	20.0	3.48	2.38	20.3
10.00	5.00	20.0	7.30	9.56	20.0
1.00	4.00	20.0	1.06±0.15[a]	4.04±0.10[a]	21.3±0.8[a]

[a]Mean and estimated standard deviation for five replicate titrations.

DISCUSSION

The analytical technique developed in this project is characterized by speed and convenience, especially when compared to alternative methods for determining the three anions (PO_4, SiO_2, and SO_4) in a single sample. The lower determination limits are comparable to present standard methods. The apparatus required, even for the semi-automatic titration, is not extremely costly, i.e., an atomic absorption spectrometer and an infusion pump. The first of these items is already part of the equipment of many water and waste water laboratories. Several of the advantages of atomic absorption are thus made available for these common important anions. An additional advantage is that since procedurally the method is a titration, the demands on the spectrometer are not high, i.e., only changes in signal are observed. Hopefully instrument suppliers will exploit these features to provide a relatively low cost unit which will allow for determination of magnesium and other common metals by atomic absorption or emission and these anions by AAIT.

The apparatus used in the method is suitable for automation. Although a beginning in the procurement of equipment for this task was possible under the budgetary limitations of the project, this effort is not yet complete.

At least two benefits of the program to chemistry have occured. One is that AAIT provides a new tool for observing inhibition processes in flame spectrometry. This provides elucidation of inhibition mechanisms.[7] In general these studies have shown that the inhibition processes are rate determined processes as opposed to solution equilibrium regulated processes. Finally, it should be noted that, although the method is based on inhibition effects, it is not an indirect method but rather employs the procedural advantages of direct titrations and atomic absorption measurements.

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LIST OF PUBLICATIONS

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"The Determination of Sulfate by Atomic Absorption Inhibition Titration," R. W. Looyenga and C. O. Huber, Analytica Chimica Acta, 55, 179-183 (1971).

"Determination of Phosphate, Silicate, and Sulfate in Natural and Waste Water by Atomic Absorption Inhibition Titration," C. I. Lin and C. O. Huber, Analytical Chemistry, 44, 2200-2204 (1972).

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